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(54) Title: THIN WALLED SILICON CARBIDE TUBE HAVING LOW WALL THICKNESS VARIATION

(57) Abstract

This invention relates to a drain cast silicon carbide ceramic tube characterized by a length (measured along the tube), a wall thickness, and an outer diameter, the ratio of the tube length to the outer diameter being at least 100:1, wherein the tube has a wall thickness variation of no more than about 0.3 mm/m.

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THIN WALLED SILICON CARBIDE TUBE HAVING LOW WALL THICKNESS VARIATION

BACKGROUND OF THE INVENTION

Because of its superior high-temperature strength, stiffness and purity, silicon carbide has been selected as the material of construction for many high-temperature applications such as injector tubes and thermocouple shield tubes. These tubes are typically made by either extrusion or slip casting. In conventional slip casting, an ionically deflocculated slip is poured into a cored porous plaster mold, allowed to cast for a set period and then drained from the mold when a predetermined thickness of slip has cast against the mold wall. Although this conventional method of slip casting silicon carbide tubes (often called "drain casting") has successfully produced tubes having an outside diameter ("OD") of at least 12 millimeters ("mm") and walls as thin as 3 mm, there is now a demand for even smaller OD, thinner walled tubes. Unfortunately, conventional slip casting has not yet reliably produced these thinner walled tubes. In particular, it was found that when a conventional slip was poured into a porous plaster mold having an annular core measuring 60 inches (1524 mm) in length and an outer diameter ("OD") of 8 mm, the bottom portion of the slip would fully cast before the length of the core was even filled with slip, thereby negating the wall thickness tailoring capability provided by drain casting.

Conditioning the above-noted mold allowed the slip to cast a tube having the desired length and OD, but the variation in wall thickness of this tube was found to be undesirably high, i.e., between 0.5 mm/m and 0.8 mm/m (wherein "wall thickness variation" is found by measuring the wall thickness at the top and bottom of the tube, calculating the difference therebetween, and dividing by the length of the tube.

Conventional methods of extruding silicon carbide thin walled tubes can produce only straight tubes and so are highly limited in application.

Accordingly, there is a need f r an optionally-curved, slip cast (or "drain cast") silicon carbide tube having a length (measured along the length of the tube) of at least

about 1200 mm and outer diameter of no more than about 8 mm, wherein the tube has a desirably low variation in wall thickn ss.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a drain cast silicon carbide ceramic tube characterized by a length (measured along the tube), a wall thickness, and an outer diameter, the ratio of the length to the outer diameter being at least 100:1,

wherein the tube has a wall thickness variation of no more than about 0.3 mm/m.

~~In one preferred embodiment, the tube has a length of at least about 1200 mm, an outer diameter of no more than about 8 mm, and an average wall thickness of between about 1.1 mm and about 1.6 mm.~~

In a second preferred embodiment, the tube has a length of at least 1200 mm, an outer diameter of no more than about 6 mm, an average wall thickness of between about 0.4 mm and about 0.9 mm, and a wall thickness variation of no more than about 0.25 mm/m.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that a sterically deflocculated silicon carbide slip provides a casting rate through a porous plaster mold which is slow enough to allow uniform, controlled casting of silicon carbide tubes. Accordingly, slip cast silicon carbide tubes having thin, small diameter walls with a lower wall thickness variation than previously known can now be made.

Without wishing to be tied to a theory, it is believed that casting conventional ionic deflocculated slips could not provide the desired thin walled tubes because those slips fail to maintain a proper level of electrostatic charge during casting. In particular, ionic deflocculation relies upon diffuse double layers (made up of negatively charged silicon carbide particles and positively charge sodium ions) to provide enough interparticle repulsion to maintain slip stability. Howev r, since calcium cations from the mold diffuse into the slip during casting, and it is known that diffuse double layer r pulsion weakens within increasing electrolyte str ngth, the

stability of an ionically deflocculated slip is typically not maintained during casting. Once the slip is destabilized, it quickly casts when it is poured into the core f the porous plaster mold. Since the slip contacts the bottom of the core for a longer time than the top of the core, the wall thickness of the cast tube is larger at the bottom of the tube.

Again without wishing to be tied to a particular theory, it is believed that the sterically deflocculated slips of the present invention escape the problems faced by the conventional ionically deflocculated slips because they do not rely upon an electrostatic charge to stabilize the slip. Steric deflocculants are surfactants which attach to the silicon carbide particles by physical or chemical means, not electrostatic means. The molecules of these surfactants have one end which has an affinity for silicon carbide and another end which has an affinity for water. Accordingly, when added to a silicon carbide slip, the surfactants coat the silicon carbide particles with their "silicon carbide-philic" ends and extend into the water with their hydrophilic ends. The hydrophilic ends provide a steric barrier which physically hinders other silicon carbide particles, especially similarly coated silicon carbide particles, from approaching and in doing so also weakens van der Walls attractive forces between the silicon carbide particles. Moreover, since the overall electrolyte concentration does not affect the surfactants' affinities nor its steric hinderance capabilities, the slip remains stable even after calcium ion influx and so does not readily floc against the walls of the porous plaster mold during casting. Since it does not readily floc, it casts very slowly. The slow casting rate makes the slip suitable for controlled casting of thin walls.

Moreover, because the casting is sufficiently slow, ordered casting is promoted and high strength and high density are achieved.

Accordingly, in some preferred embodiments, there is provided a novel process for making thin walled tubes comprising the steps of:

a) preparing a slip comprising silicon carbide powder, a liquid carrier and a steric deflocculant,

b) preparing a porous plaster mold having an annular core characterized by a length and an outer diameter, the ratio of the length to the outer diameter being at least 100:1,

c) pouring the slip into the core of the porous plaster mold,

d) casting the slip to produce a silicon carbide tube having a wall thickness variation of no more than 0.3 mm/m, and

d) draining the slip from the core.

The steric deflocculants used to make the present invention include any surfactant molecule having a first end which has an affinity for silicon carbide and a second end which has an affinity for water. Some suitable steric deflocculants include polyethyleneimines and other suitable organic surfactants. In preferred embodiments, PS-2, a polymeric dispersant available from ICI Specialty Chemicals of Wilmington, Delaware is used. Typically, the steric deflocculant is added to the slip in an amount of about 0.4-1.0 weight percent ("w/o") of the liquid carrier.

The silicon carbide powder of the present invention typically comprises a bimodal distribution comprising between about 45 w/o and about 55 w/o coarse SiC grains with a particle size ranging from 10 to 100 microns ("the coarse fraction"), and between about 45 w/o and about 55 w/o of a fine SiC grain with a size distribution of between 1 and 4 microns ("the fine fraction"). Preferably, the fine fraction has an average particle size of about 2-3 microns ("um") and the coarse fraction has an average particle size of about 60 microns.

Other components of the slip typically include a liquid carrier, preferably water, present in an amount of from about 12 w/o to 16 w/o solids, and acrylic binder present in the range from about 0.25 to 1.0 w/o solids.

In one sp cially preferr d embodiment, a silicon carbide mixture consisting of about 48 w/o green silicon carbid having an average siz of about 60 microns and about 52 w/o gr en

silicon carbide having an average size of 2-3 microns is prepared. Water is then added to provide a slip having a viscosity of between about 500 and about 750 cps. Steric deflocculant PS-2 is added in an amount of about 0.7 w/o of the water. An acrylic latex binder is also added in an amount of about 0.25 w/o of the solids. These components are mixed in a ball mill which has been evacuated to vacuum level of between about 27 and 30 inches Hg and milled for at least about 17 hours.

Concurrently, a plaster mold with a 70% consistency is prepared and an annular core is provided therein having a length of about 1542 mm (60 inches) and a diameter of about 6-8 mm. The bottom of the core is then capped and the slip is poured into the cavity. Casting time is dependent on both desired wall thickness and slip viscosity. At a desired viscosity of 750 cps and required nominal wall thickness of about 6-8 mm, the slip is allowed to remain in the mold 14-18 minutes. At that time, the cap is removed and the slip drains from the mold.

After the slip has been drained, a small amount of de-ionized water can be poured down the cavity of the casting to insure a lump free drained surface. The cast part is allowed to dry in the mold for 20-30 minutes. After that time, the mold is disassembled and the tube is removed by using an appropriate stripping fixture. This fixture simulates the outside shape of the cast tube, thereby enabling it to remain dimensionally correct during drying.

The cast tube is then allowed to air dry overnight or oven dry for a suitable period prior to green finishing. The cast tube is cut to length (if desired) and final finishing may be performed.

The cast tube can now be fired. The initial firing step is conducted in a furnace under conditions typical for silicon carbide recrystallization. After this initial firing, the tube is prepared for one of two possible final firing steps which is dependent on part size and intended application. This second firing st p consists of either impregnating with silicon to eliminate p rosity or CVD coating with silicon carbide, ach

according to conv ntional means. After this second firing, the part is machin d to its final dimension.

Silicon carbide ceramic tubes typically having lengths of at least 1200 mm, often betw en 1200 and 1500 mm, and sometimes at least 2000 mm can be made in accordance with the present invention. These tubes typically have outer diameters of between about 4 and about 8 mm, usually no more than 6 mm, and often between 4 and 6 mm. The ratio of the tube's length to its outer diameter is typically between 150:1 and 500:1, more often between 150:1 and 250:1. In addition, the average wall thickness is typically between about 0.4 mm and about 1.6 mm, and wall thickness variations are typically no more than 0.3 mm/m, and are usually between about 0.25 mm/m and about 0.3 mm/m, and are sometimes no more than 0.25 mm/m.

A cast, unfired body produced in accordance with the above especially preferred embodiment typically exhibits a bulk density of at least about 2.75 g/cc and a four point bending strength of at least about 5 MPa. Its pore size typically ranges from about 0.1 to about 4 microns. Its average pore size is typically about 0.4 microns. Its fired room temperature 4 point flexural strength is typically about 300 MPa, and its fired 1200°C flexural strength is typically about 375 MPa.

Analysis of the variation in wall thickness was measured in tubes made in accordance with the above embodiment. Tubes having about 1254 mm (60 inch) lengths and about 8 mm outer diameters (to provide a length-to outer diameter ratio of 156:1) were cast in about 18 minutes to provide an average wall thickness of between about 1.1 mm and about 1.6 mm, with a wall thickness variation of about 0.3 mm/m. Tubes of similar length having about 6 mm outer diameters (to provide a length-to outer diameter ratio of 209:1) were cast in about 14 minutes to provide an average wall thickness of between about 0.4 mm and about 0.9 mm, with a wall thickness variation of about 0.25 mm/m.

~~The novel recrystallized silicon carbide ceramics of the present invention may be used in conventional siliconized silicon carbide or CVD coated silicon carbide applications, including those applications disclosed in US Patent No.~~

3,951,587, the specification of which is incorporated by reference.

For the purposes of the present invention, a "drain cast" SiC ceramic includes products made by drain casting, slip casting or pressure casting, wherein the products possess a relatively smooth surface and isotropic grain orientation. Accordingly, "drain cast" products do not include injection molded SiC ceramics, which are characterized by striations along the surface of the extrudate and preferential grain orientation.

I claim:

1. A drain cast silicon carbide ceramic tube characterized by a length (measured along th tube), a wall thickness, and an outer diameter, the ratio of the tube length to the outer diameter being at least 100:1, wherein the tube has a wall thickness variation of no more than about 0.3 mm/m.
2. The tube of claim 1 having a length of at least about 1200 mm and an outer diameter of no more than about 8 mm.
3. The tube of claim 2 having an average wall thickness of between about 1.1 mm and about 1.6 mm.
4. The tube of claim 3 wherein the ratio of the tube length to the outer diameter is between 150:1 and 500:1.
5. The tube of claim 4 wherein the ratio of the tube length to the outer diameter is between 150:1 and 250:1.
6. The tube of claim 1 having a length of at least about 1200 mm and an outer diameter of no more than about 6 mm.
7. The tube of claim 6 having an average wall thickness of between about 0.4 mm and about 0.9 mm.
8. The tube of claim 7 having a wall thickness variation of no more than about 0.25 mm/m.
9. The tube of claim 8 wherein the ratio of the tube length to the outer diameter is no more than 500:1.
10. The tube of claim 9 wherein the ratio of the tube length to the outer diameter is no more than 250:1.
11. A process for making thin walled tubes comprising the steps of:
    a) preparing a slip comprising silicon carbide powder, a liquid carrier and a steric deflocculant,
    b) preparing a porous plaster mold having an annular core characterized by a length and an outer diameter, the ratio of the length to the outer diameter being at least 100:1,
    c) pouring the slip into the core of the porous plaster mold,
    d) casting the slip to produce a silicon carbide tube having a wall thickness variation of no more than 0.3 mm/m, and

d) draining the slip from the core.

12. Th process of claim 11 wherein the liquid carrier is water.

13. The process of claim 12 wherein the steric deflocculant is a polyethyleneimine.

14. The process of claim 13 wherein the polyethyleneimine is PS-2.

15. The process of claim 13 wherein the steric deflocculant is present in the slip in an amount of between about 0.4 w/o and about 1.0 w/o of the water.

16. The process of claim 11 wherein the core has a length and a diameter such that the ratio of the length to the diameter is between 150:1 and 250:1.

17. The process of claim 16 wherein the core has a length of at least 1200 mm and a diameter of no more than 8 mm.

18. The process of claim 16 wherein the core has a length of at least 1200 mm and a diameter of no more than 6 mm.

19. The process of claim 17 wherein the tube has an average wall thickness of between 1.1 mm and 1.6 mm.

20. The process of claim 18 wherein the tube has an average wall thickness of between 0.4 mm and 0.9 mm.

INTERNATIONAL SEARCH REPORT

Inter...onal Application No
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A. CLASSIFICATION F SUBJECT MATTER
IPC 6 C04B35/565 C04B35/634

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	P. VINCENZINI: "High Tech Ceramics, Part A" 1987 , ELSEVIER , AMSTERDAM, NL XP000600966 see page 623 - page 632 ---	1-20
A	EP,A,0 486 938 (ASAHI GLASS COMPANY LTD., ET AL.) 27 May 1992 see page 5, paragraph 1; examples 1,C-1 -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
9 September 1996	27.09.96

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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